OCT 1987

INVENTORY OF HEAVY METALS DATA:
LOUISIANA COASTAL ZONE

COASTAL ZONE
INFORMATION CENTER

TD 196 .M4 T5 Submitted by

Marty E. Tittlebaum

Department of Civil Engineering
Louisiana State University
Baton Rouge, LA 70803

Submitted to

John deMond, Project Manager Louisiana Department of Natural Resources

TABLE OF CONTENTS

•

																					Page
1.	INTRODUCT	ION		•				•		•		•	•	•	•	•		•	•	•	1
2.	DATA COLL	ECTION .		•			•	•	•	•	•	•	•	•	•	•	•	•	•	•	2
3.	ASSESSMEN	T OF DATA		•	•		•	•	•		•	•	•	•	•		•	•	•	•	3
4.	RECOMMEND	ATIONS .			•		•	•	•	•	•	•	•	•				•	•	•	· 15
5.	REFERENCE	s		•	•		•	•	•		•	•	•	•			•	•	•	•	23
6.	BIBLIOGRA	рну		•	•		•	•	•	•	•	•	•	•	•	•	•	•	•	•	27
7.	APPENDICES																				
	A 1:250,000 Location Maps (separate document six total) B Data Printout, Software and Instructions (separate document)																				
	C Excursions from USGS Sediment Alert Level and Statewide Order 29-B Limitations																				

1. INTRODUCTION

During the past five years, there have been numerous, independent reports of heavy metal contamination in Louisiana's aquatic ecosystems. The Louisiana Department of Environmental Quality has most recently investigated metal contamination in sediments of Bayou Trepaigner, Calcasieu River, Caddo Lake and Devil's Swamp. Louisiana State University researchers (Tittlebaum and White, 1983) found heavy metal enrichment in a Baton Rouge urban lake and two waterways in New Orleans. In a 1984 feasibility study, the U.S. Army Ccrps of Engineers suggests that heavy metals from the Mississippi River and its sediments may serve as possible contaminants for the hydrologic basins receiving fresh-water diverted from the Mississippi for the purposes of retarding salt water intrusion into delta plain estuaries and marshes. In a 1981 Environmental Impact Statement, the U.S. Coast Guard recommends that the State consider constructing a bridge on a stretch of U.S. Highway 90 near Morgan City, rather than a ground-level highway, to prevent the release of mercury from sediments disturbed by dredging operations.

Toxic heavy metals such as zinc, cadmium, lead, mercury and arsenic are potential health hazards in at least a few known locations in Louisiana. Heavy metals tend to accumulate in Louisiana's highly organic bottom sediments, from which they can be remobilized and move up to biologic food chain, affecting valuable aquatic resources as well as human health.

The Office of Conservation of the Louisiana Department of Natural Resources (DNR) has enacted new regulations governing oil field waste disposal in wetland environments. Disposal techniques include landfarming which is intended to dispose of trace metal-bearing muds and

fluids without increasing the level of these metals above acceptable standards. This approach will be reviewed on a case-by-case basis by the DNR Coastal Management Division (CMD) for every oil field waste disposal pit in the coastal zone. To properly assess each project, CMD must have a significant amount of widely varying information including background levels of trace metals in coastal ecosystems.

This report provides an inventory of existing sediment trace metal data in a format that enables CMD coastal resource analysts to retrieve and use it. It also identifies data deficiencies which may be the basis for subsequent joint studies by CMD and the Office of Conservation to remedy data gaps and increase the understanding of trace-metal mobility in coastal environments.

2. DATA COLLECTION

The primary objective of this study is to compile an inventory of heavy metals data for Louisiana coastal sediments which can be obtained from published and unpublished sources. It is not the intent of this project to investigate the severity of metal contamination in a detailed, site specific manner. This would be especially difficult without compiling data describing natural background levels of heavy metals in Louisiana sediments. Rather, the intent is to compile data in a format which will provide regulatory personnel within CMD with all available sediment data relating to heavy metals for use in permit processing. The compilation of data includes the following heavy metals:

Aluminum	Cobalt	Nickel
Aluminum	CODAIL	NICKEI
Arsenic	Copper	Selenium
Barium	Iron	Silver
Beryllium	Lead	Vanadium
Cadmium	Manganese	Zinc
Chromium	Mercury	

During the data collection phase of the project, the researchers developed a listing of the sources of all data obtained and a set of maps showing the locations of the sampling stations for which data was reported.

The study area defined by this project included twenty-one parishes located in the Louisiana coastal zone; generally south of Highway I-10 (see Appendix A). Data from Jefferson County, Texas, was also included in the study. Listed below are the included parishes:

Ascension Orleans Assumption Plaquemines St. Bernard Calcasieu Cameron St. Charles St. James Iberia St. John Iberville Jefferson St. Martin Jefferson Co., TX St. Mary Jefferson Davis St. Tammany Lafayette Terrebonne Lafourche Vermillion

The appropriate state agencies that were contacted for heavy metals data include the Department of Wildlife and Fisheries, Department of Transportation and Development, Department of Natural Resources, and Department of Environmental Quality.

Also contacted were the following Federal agencies: U.S. Environmental Protection Agency, Region 6; U.S. Environmental Protection Agency, Office of Water Regulations, Washington, DC; U.S. Army Corps of Engineers, New Orleans District; U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS; U.S. Coast Guard; U.S. Geological Survey, Baton Rouge; U.S. Department of Wildlife and Fisheries, Slidell, LA; National Space Technology Lab, Bay St. Louis, MS; USGS, Minerals Management Service, Metairie, LA.

The universities contacted for metals data were Louisiana State University, Baton Rouge; University of New Orleans; Tulane University; University of Southeast Louisiana; Southwestern Louisiana State University; Nichols State University; Texas A & M; and University of South Alabama.

Inquiries were made to laboratories, engineering firms, environmental companies and groups in the New Orleans and Baton Rouge areas for non-proprietary heavy metals data. Requests were made to chemical companies and petroleum companies for non-proprietary metals data. These companies include: Texaco Oil Co., Amoco Oil Co., Freeport Chemical, Freeport MacMoran, Mobile Oil Co., Kaiser Aluminum, Exxon Oil Co., and Shell Oil Co.

A literature survey was run at the Middleton Library of Louisiana State University using NTIS (National Technical Information Service), GEOREF, oceanic abstracts, environmental bibliography, aquatic science, and fisheries abstracts data bases. A complete listing of all sources contacted is included in the bibliography.

3. ASSESSMENT OF DATA

Through the course of this study, a large amount of sediment heavy metal data was identified and cataloged into a computer software package which can be updated and used to recall the data in various forms. Data retrieval can be performed by various categories including by parish, by sample number, and by coordinates. Also, by listing coordinates, the program will identify the three nearest sample site locations and determine the distance to those sample sites.

The total number of sediment heavy metal sample sites identified is 395. Many of these sites had multiple sampling dates associated with

them, yielding a total of 708 sample sets. Each set has one or more sediment metal concentrations for the previously listed metals.

Specific operating instructions and program listing are included in Appendix B together with a printout of all data identified.

Assessment of this large data bank was limited to two specific areas of interest: biological accumulation of metals by aquatic life forms and a state-wide summary of findings. The summary of findings includes the identification of excursions from USGS sediment levels and state-wide order 29-B limitations (Appendix C).

A. Biological Accumulation of Metals by Aquatic Life Forms

The presence of toxic contaminants in terrestial and aquatic food chains has been a major cause of concern due to the potential chronic or acute harmful effects on living organisms. Many chemicals are frequently present in the environment in extremely low concentrations, often below the levels readily detectable by chemical and physical analytical techniques. Aquatic organisms can readily absorb metals from their surroundings, and may accumulate levels that are greatly in excess of the ambient concentrations in their environment. Table 1 indicates concentrations above ambient levels in aquatic species sampled in Vermillion Parish.

It is the ability of aquatic species to regulate abnormal concentrations that determines tolerances, and is a critical factor in survival. However, there is an upper limit to the amount of metal which can be excreted by animals, above which there is an accumulation in body tissues.

The initial uptake of metals by aquatic organisms can be considered in terms of three main processes: (1) from water through respiratory

Table 1. Concentrations above ambient levels in aquatic species sampled in Vermillion Parish (11).

Arsenic	
Clams	6-15x
Fish	up to 17x
Cadmium	
Zooplankton (microscopic animals)	6,000x
Oysters	2,150x
Clams	30 - 2,260,000x
Chromium	
Oyster	60,000
Clams	200 to 1,050x
Lead	
Zooplankton	197,000
Oysters	3,300
Clams	5,300
Mercury	
Plankton (microscopic plants)	20 - 100
Shrimp	20 - 55
Oysters	500 - 2,800
Clams Fish	1,223 250
Insects	8,310
Silver	
0,,,,,,,,,,,	18,700
Oysters Clams	2,300
Fish	120
Zinc	
Zooplankton	5,100
Algae	64,000
Oysters	750,000
Shrimp	5,600
Crabs	5,800
Fish	16,300
Marsh Grass	880

surfaces (e.g., gills), (2) adsorption from water onto body surfaces, and (3) from ingested food, particles, or water through the digestive system.

In the case of photo- and chemoautotrophic organisms, metal uptake occurs directly from solution, or for higher plants additionally via the roots. For many metals, rates of absorption are directly proportional to the levels of availability in the environment.

Metal uptake from dietary sources in comparison to direct adsorption from solution is of fundamental importance with heterotrophic aquatic organisms. Available evidence is limited but indicates that food and particulates are more important sources of metals than water, for large animals such as fish and lobster. Within polluted aquatic environments dietary preferences or feeding habits are significant because of metal enrichment in sediments, particulates and detritus.

Bioconcentration of a metal is a complex process dependent not only on the chemical parameters of the medium, but also on the physical structure, i.e., size, sex, age, lipid storage and metabolism of the biota, as well as species and half life of the metal. Data shows that once absorbed, some metals are retained for long periods before being flushed out of the system.

Metals have been placed into four different classes according to their bioconcentration factor (BCF):

Class	BCF
Non-Accumulative	< 60
Slightly Accumulative	60 - 70
Moderately Accumulative	700 - 800
Highly Accumulative	> 8000

Table 2 shows the BCF's and half lives for most of the metals identified in the study. There is no appreciable bioaccumulation for beryllium, chromium, nickel, selenium and silver; as the BFC's were less than 400. Arsenic, cadmium, copper, lead, mercury and zinc show a high degree of bioaccumulation.

Chronic low dose (sublethal) exposure to heavy metals can lead to changes in the histology or morphology of the tissues in fish and crustacean species. These changes are secondary effects due to interference with enzyme processes involved in food utilization.

Supression in growth, reproduction circulation and respiration are noted after exposure to relatively low metal concentrations. Reproduction in many aquatic organisms is affected in the parts per billion range for most aquatic toxic metal ions. Changes also occur in blood chemistry, endocrinology and enzyme activity after uptake or sublethal quantities of metals. The observed behavioral changes are the impairment of feeding and learning processes, swimming, and response to external stimuli.

Studies of the community structure (species richment, species composition and abundance) or epibenthic seagrass fauna show a decrease of 20 common species, mostly fish, which were correlated with the concentration of contaminant metals (Cd, Cu, Pb, Mn and Zn) in the sediments. It was also found that the frequencies of certain species, mostly crustaceans, correlated with particle size distributions. Both contaminant metals and sediment particle size have substantial controlling effects on the community structure. Heavy metals show a greater effect on fish than crustaceans. Opportunistic epibenthic species avoid a contaminated area.

Table 2. BCF's and Biological Half-Lives for Inorganic Contaminants (28).

Contaminant	BCF	Biological Half-Life	Source of Information
Arsenic	0-450	10-60 days	Waldichuk (1974; Woolson et al. (1976); Gidding & Eddleman (1977); U.S. EPA (1979
Beryllium	5-150	37-53 days	U.S. EPA (1979)
Cadmium	3-182,000	10-30 years	Waldichuk (1974; U.S. EPA (1979; Piotrowski & Coleman (1980); Friberg et al. (1974)
Chromium (trivalent)	1-152	616 days	U.S. EPA (1979
Cooper	0-35,000	very short	Waldichuk (1974); Weber (1977); U.S. EPA (1979)
Lead	42-100,000	10 years	Waldichuk (1974); U.S. EPA (1979)
Mercury (inorganic)	129-33,800	40-70 days	Waldichuk (1974); Weber (1977); U.S. EPA (1979); Piotrowski and Coleman (1980)
Nickel	918-61	very short	U.S. EPA (1979)
Selenium	2-20	1-several days	U.S. EPA (1979)
Silver	0-368	15-52 days	U.S. EPA (1979)
Zinc	1-27,080	200-400 days	U.S. EPA (1979)

^{*}BCF's reported are for both freshwater and marine oranisms. Biological half-life is the estimated time for excretion of 50% of the total ingested metal from the biological system.

Several general characteristics of metal toxicity within aquatic organisms can be expressed:

- (1) Metal ions and complexes exhibit a wide range of toxicity to marine and freshwater organisms.
- (2) In fish, the rate of absorption of methyl mercury is faster than that for inorganic mercury (bacteria are capable or transforming inorganic mercury compounds into dimethyl and methyl mercury), and the clearance rate is lower, with a net result of high methyl mercury concentrations in the muscle tissue.
- (3) Among the metals, cadmium is one of the most readily absorbed and accumulated in plants grown in contaminated soil.
- (4) The biologic methylation or inorganic lead to tetramethyl lead by lake sediment microorganisms has been demonstrated, but the significance of this observation remains uncertain.
- (5) Bioaccumulation of arsenic species occurs readily in some aquatic organisms. Seaweeds, freshwater algae and crustaceans accumulate significant amounts of arsenic. The ambient water concentration (FDA) for arsenic is suggested to be zero to protect human health from potential carcinogenic effects of arsenic exposure through ingestion of water and contaminated aquatic organisms.
- (6) Silver is toxic to humans and aquatic organisms at very low concentrations. Once absorbed by living tissues, silver is not readily removed and tends to accumulate.
- (7) In general, mollusca, crustaceans, oliqochaetes and leeches appear to be the most sensitive taxa to zinc.

B. State-Wide Summary

In order to evaluate and summarize the sediment heavy metal data identified during this study, it is necessary to view the data in two different manners; specific concentrations of heavy metals in sediments and overall location of the sampling sites. The concentrations of metal in sediments is compared with two sets of limitations; USGS and USEPA Region 6 alert levels in sediments, and Statewide Order No. 29-B heavy metals limitations. These are listed in Tables 3 and 4, respectively. The overall location of sample sites is best determined by perusal of the data maps (Appendix A).

The following general comments can be made based upon the data listings, the prepared maps and the listings of excursions from the sediment alert levels and 29-B limitations. East of Michoud in Orleans parish there is a cluster of samples taken along the Gulf Intracoastal Waterway, and in feeder tributaries. Of the nine samples taken in this cluster, eight exceed some parameter of the 29-B limitations. Of the twelve sites sampled in Lake Pontchartrain, all exceed 29-B background limits.

Random samples were taken along the Mississippi River Gulf Outlet in St. Bernard Parish; from mile 0 to approximately mile 50. At mile 20 there is a cluster which extends from the north and south sides of the channel bank out into Chandeleur and Breton Sounds. A majority of these samples exceed 29-B limits. Sites in Plaquemine Parish are also in waterways; a cluster is noted at the mouth of Southwest Pass. All wetland samples at one site of a proposed freshwater diversion structure exceed limitations in 29-B.

Table 3. Toxic Criteria and Alert $_{1}^{1}$ Levels for Metals in Freshwater and Sediments

	USGS Alert Levels	Region 6 Alert Levels
Parameter	in Sediments (ug/kg)	for Sediment (ug/l) Interstitial/Elutriate)
Antimony	500,000	-
Arsenic	200,000	440 (As ⁺³)
Barium	2,000,000	-
Beryllium	200,000	-
Boron	-	-
Cadmium	20,000	24 hr. Avg.
Chromium	200,000 (t)	Max. level 0.29
Copper	2,000,000	5.6
Cyanide	100,000	3.5
Iron	-	-
Lead	500,000	24 hr. Avg.
Manganese	-	-
Mercury	20,000	.2
Nickel	2,000,000	24 hr. Avg.
Selenium	20,000	35 [*]
Silver	1,000,000	Max. level
Thallium	-	-
Zinc	5,000,000	47

⁽t) = total chromium

^{*}as inorganic selenite

Compiled from DRAFT, Arkansas, Oklahoma, Louisiana, New Mexico, and Texas, Environment Protection Agency, Region 6, Sediment Alert Levels

Table 4. State-Wide Order 29-B Limitations for all Pit Closures and Solidification.

Mixtures	for Waste/Soil for all Pit Techniques	Leachate Testing (EP Toxicity) for Solidification			
Parameter	Limitation (ppm)	(mg/			
Arsenic	10	Arsenic	<u><</u> 0.5		
Barium	2,000	Barium	< 10.0		
Cadmium	10	Cadmium	< 0.1		
Chromium	500	Chromium	<u><</u> 0.5		
Lead	500	Lead	<u><</u> 0.5		
Mercury	10	Mercury	<u><</u> 0.02		
Selenium	10	Selenium	<u><</u> 0.1		
Silver	200	Silver	<u><</u> 0.5		
Zinc	500	Zinc	<u><</u> 5.0		

Coverage in Jefferson Parish is in waterways only. The majority of samples taken along Barataria Bay waterway exceed some parameter of the 29-B limitations. Coverage in St. Charles, St. James, St. John the Baptist, Ascension, Jefferson Davis and Lafayette Parishes can be considered non-existent as none of these parishes has more than 4 samples parishwide; and for the most part, samples were taken in water courses only.

All places sampled along the Gulf Intracoastal Waterway in Lafourche and Terrebonne Parishes exceed metal limits for 29-B. The coastal wetland between Jefferson Parish and the Atchafalaya River lack coverage. There are a few samples in small clusters in this area in waterways. One cluster, at the head of the Houma navigation canal and the Gulf Intracoastal Waterway exceeds the 29-B limits. Samples along the Atchafalaya River channel in the Atchafalaya Bay, and samples in Grand Lake, Six Mile Lake, Lake Palourde and Flat Lake also exceed 29-B. Two of the eleven samples in Lake Verret exceed 29-B limits. One sample, Sa.6, exceeds USEPA Region 6 alert levels for cadmium. This is apparently a bad sample as the cadmium levels at th same site for dates previous to, and after the "excess" sample taken, were in an acceptable range.

A cluster of eleven samples in the Gulf, Southwest of Chenier au Tigre in Vermillion Parish exceed the limitations of 29-B. Also in the Gulf, the cluster of samples to the south of the old and new Mermentau River channel outlets exceed 29-B. Thirteen of twenty-one samples taken from the Calcasieu Ship Channel, starting at the beginning of the dredged channel to north of Rabbit Island in Calcasieu Lake exceed limits of 29-B. Also above 29-B are samples in the site clusters at Moss Lake

and site clusters at Lake Charles. Jefferson Davis Parish with three sites and Iberville Parish having six sites were the only two parishes of the twenty-one parishes surveyed that contained sites which did not exceed the 29-B limitations.

There is a gross lack of complete parish wide coverage in sampling for metals. Most of the sites were either clustered or at intervals along navigable waterways taken in conjunction with dredging activities. The majority of land area was devoid of any sample sites whatsoever. There is not a consistency of metal specie sampled. Generally, data from storet shows the same metals sampled for each site, but variations in metals do occur. Data from non-federal government agencies or private firms usually sample for only a very limited number of metals. More rapid sedimentation and scour occurs in outlet channels and swift flowing rivers, therefore data in these areas may not be considered valid if not updated on a regular basis.

4. RECOMMENDATIONS

As previously stated, the primary objective of the research effort was to compile an inventory of heavy metals data for the Louisiana coastal sediments. It was not the intent of this study to investigate the severity of metal contamination in the Louisiana coastal zone or to review and evaluate Statewide Order No. 29-B with regard to storage, treatment and disposal of nonhazardous oilfield wastes. Based upon the acquisition of the included sediment heavy metal data and the assessment of that data with regard to deficiencies, it was felt that a brief discussion of number of observations and/or recommendations would be appropriate. These discussions fall into four general categories:

- (1) Additional data modification and updating needs directly relating to this report.
- (2) Statewide Order No. 29-B pit closure techniques and onsite disposal of nonhazardous oilfield wastes.
- (3) Heavy metal contamination in sediments.
- (4) Knowledge-based (expert) systems technology for identification of economic and environmentally sound disposal methods.

With regard to data modification and updating needs, there are recommendations relating to the developed software package, data file and maps. The maps indicate the location of each sample site identified. The usefulness of these maps to regulatory officials and industry representatives would be significantly increased if overlay sheets with disposal pits locations were added. This would enable interested parties, either closure plan reviewers or pit owners, to see where the available sediment data is in relation to existing or planned waste pits. It would also make areas which are deficient in available or appropriate sediment data, in relation to disposal pit locations, readily identifiable.

In order to make the data system more useful and applicable, a regularly scheduled updating of the data base should be performed. This would add data from on-going or future studies and may include new sampling sites or additional results from existing sample locations. In addition, the method of identifying the location of the oilfield waste pits and the sediment sampling location needs to be standardized. The vast majority of available data is located by coordinates, whereas waste pits are often located by identification of township, section and range.

Most importantly, the usefulness of the developed data base is directly related to how successful DNR is in identifying and informing potential users of its existence and capabilities.

With regard to Statewide Order No. 29-B, only a brief discussion of recommendations will be included in this report as this is beyond the scope of this study. In general, it can be stated that 29-B has established an excellent framework for the regulation of treatment and disposal of nonhazardous oilfield wastes. However, there are some needs that should be addressed in order to enhance it implementation. The following comments deals solely with Sec. XV, paragraph 2.7, "Pit Closure Techniques and Onsite Disposal of NOW".

Since the selection of a treatment and disposal technique for an oilfield waste pit greatly depends upon the heavy metal content of the pit and metal content of the background sediments, specific requirements with regard to sampling techniques and locations should be addressed. As can be seen from the sediment data presented in this report, additional data collection may be a necessity in many cases. Decisions will need to be made regarding acceptable distance from a waste pit to available background data. Also specific guidelines need to be listed regarding how and where pit and background sediment samples are obtained. Are samples collected at the surface or are samples composites with depth? What is a sufficient distance from the waste pit for a background sample to be taken? At what distance does the sample no longer relate to the background conditions of the pit? These questions need to be addressed.

These questions also relate to the need for the regulations to define who is responsible for data collection if there are data

deficiencies. As previously discussed, major deficiencies do exist in the data and guidance will be necessary to determine what additional data needs to be collected.

Finally, the actual feasibility of utilizing the proposed closure techniques needs to be evaluated. It would appear that in the Louisiana coastal zone, burial or trenching and solidification are not feasible alternatives because of the ground water table requirements. Also, end product requirements for different on-site treatment alternatives need to be standardized. Examples are that solidified wastes must meet compressive strength and permeability limitations, but other treatments do not. Additionally, solidified wastes must meet leachate testing limits when other closure methods do not. It is felt that by defining the specific objectives of 29-B that treatment performance criteria can be easily defined.

It is widely known that bottom sediments, either in fresh or salt water, act as accumulators of pollutants, particularly heavy metals. Pollutant concentrations several hundreds or thousands of times the overlying water concentration can result. Problems with polluted sediments arise because, first, these sediments (particularly in the coastal zone) are the habitats for many commercial fisheries species, either for part or all of their life cycle. Second, as bottom sediments are eroded and moved, either naturally or through man induced processes such as dredging, the sediments may act as a source of concentrated pollutants for aquatic organisms and ultimately humans. Finally, the ability to determine the significance and degree of heavy metal contamination in bottom sediments is essentially limited to the comparison of absolute metal concentration values alone, which does not account for

the many physical and chemical sediment parameters that influence sediment metal concentration values.

The Louisiana coastal zone is an area containing thousands of square miles of estuaries, which are among the most productive private and commercial fish and wildlife habitat areas in the nation. Excessive heavy metal contamination of these ecologically sensitive estuaries could evoke serious consequences. Initially, the more primitive organisms at the bottom of the food chain would succumb to the contamination. However, once this food chain foundation is eroded, the higher forms of life, including man, could be threatened. However, a sediment contamination threshold, distinguishing an uncontaminated sediment from a contaminated one, has not been established.

Several things are needed to mitigate the adverse effects of sediment borne pollutants. First, a knowledge of the present distribution of polluted sediments, including the areal and vertical distribution of pollutant type and amount, is needed. Second, the degree of sediment contamination must be established. Third, knowledge of the processes controlling pollutant concentrations and of the physical/chemical behavior of the adsorbed pollutants is necessary. Fourth, technology is required that will allow bottom sediment pollutants to be accurately and quickly surveyed, to make predictions of future pollutant concentrations and distribution, and to allow pollutant concentrations to be modified or controlled. With the abilities described above, a management of bottom sediment pollutants could be feasible. The problem at present is that the above abilities are not adequately in existence.

Current technologies and analytical techniques make the analysis of heavy metals in sediment a routine practice. However, the determination

of whether significant contamination exists is an unresolved problem. Metal distribution in sediments is influenced greatly by several sediment characteristics, principally grain size and organic content.

Because of these influences, dissimilar sediment types have vastly different thresholds of contamination. Currently, the acceptable method of determining heavy metal contamination in sediments involves the comparison of metal concentration values. However, in some cases, this method can be significantly influenced by a sediment's physical and chemical composition.

Presently, efforts to eliminate the influences of heavy metal distribution in sediment are met with varying degrees of moderate success. Procedures to reduce the effects of grain size and organic content on heavy metal distribution in sediment are not only time consuming, but differ widely from researcher to researcher.

In natural sediment systems, elements as well as metals exist together in fixed proportions to each other, with only minor variation. Furthermore, some metals are conservative in nature; that is, they are naturally present in soil and sediment in high concentrations and are affected minimally by man-made influences. Trace metals, on the other hand, are naturally present in small concentrations and are greatly affected by man-made influences. Ratios of trace metals to conservative elements reveal geochemical imbalances due to elevated trace metal concentrations normally associated with man-made activities.

Correlations do exist between the concentrations of several metals, especially Cd/Fe, Ni/Fe, Zn/Fe and Pb/Al. The significance of these correlations is that it shows there is a similarity between the geochemical cycles in which metals participate. It also implies that

elements should naturally exist in sediments in relatively constant proportions to one another.

Relative atomic variation, a statistical method of determining metal contamination based on regression analysis of significant element pair correlations, does not achieve the success necessary to be considered a viable alternative to the present methods used in determining metal contamination.

A better method of analyzing sediments in order to determine contamination may be in the use of metal pair concentration ratios alone or in conjunction with the more conventionally accepted method of comparing metal concentration values. Metal pair ratios can be used to determine background metal concentrations and to determine, via comparison, the existence of metal contamination in bottom sediment samples.

It is apparent that many non-hazardous oil field waste generators are becoming more confused about their legal and regulatory obligations and about how to select the technically best and most cost effective methods available for properly handling their waste problems. The use of knowledge-based (expert) system should assist generators in their decision making process, be of economic benefit to industry, and help identify environmentally sound waste management options.

Prescriptive/consultative knowledge-based systems are an appropriate means for transferring state-of-the-art treatment and disposal technology and management options to reach world applications.

Currently, the public, regulatory agencies and waste generators have difficulties in keeping abreast with the ever changing rules, regulations and technological advances of waste management. An expert system can be a useful means to help solve the problem of keeping

current with a fast changing technology and to assist regulators and generators in selecting the most environmentally safe and cost-effective waste management approach.

The development of expert systems is an advance in computer technology that has taken a special place in the toolkit of systems developers. The use of programming languages such as LISP or PROLOG or a development tool such as ROSIE offer many advantages over conventional programming. The data structures and program control structures have the same syntax and they can be easily updated without major system revisions. This is important in the area of waste management, for any expert system must be one that can be readily updated and be used by a wide range of both technical and regulatory personnel.

The prototype system could be developed and tested using both hypothetical and real situations. It would be provided to Louisiana

Department of Natural Resources and Office of Conservation staff for use and comment.

An expert system could be used to take into account a number of factors, both environmental and economic, which are presently beyond the scope of 29-B. These factors may include items such as distance to nearest permitted commercial disposal facility, risk associated with transportation, background contamination levels, etc. The use of an expert system, together with the background heavy metal data and an approach used to evaluate what the background sediment data means, will make implementation of Statewide Order No. 29-B an important part of protecting Louisiana's natural resources.

- 5. REFERENCES, COMMENT LEGEND AND LIST OF SYMBOLS
- 1. United State Geological Survey, Storet. United States Environmental Protection Agency, Washington, D.C., Oct., 1986.
- United States Army Engineers, New Orleans, District, Storet.
 United States Environmental Protection Agency, Washington, D.C.,
 Oct., 1986.
- 3. U.S. Environmental Protection Agency, Region 6, Storet. United States Environmental Protection Agency, Washington, D.C., Oct., 1986.
- 4. U.S. Environmental Protection Agency Headquarters, Storet.
 Washington, D.C., Oct., 1986 (Louisiana Data).
- 5. Texas Dept. of Water Resources, Storet. United States Environmental Protection Agency, Washington, D.C., Oct., 1986.
- Atchafalaya Bay Louisiana Sediment and Water Quality Assessment.
 Corps of Engineers, New Orleans District, New Orleans, LA, July,
 1975
- 7. Houma Navigation Canal, Louisiana, Assessment of Impacts of Maintenance Dredging on Water Quality. Corps of Engineers, New Orleans District, New Orleans, LA, July, 1975
- Barataria Bay Waterway, Louisiana, Assessment of Impacts of Maintenance Dredging on Water Quality. Corps of Engineers, New Orleans District, New Orleans, LA, July, 1975
- 9. Atchafalaya Basin East and West Access Channels and West Freshwater Distribution Channel, Assessment of Impacts of Maintenance Dredging on Water Quality. Corps of Engineers, New Orleans District, New Orleans, LA, July, 1975

- 10. Devel, Lloyd E., Jr., and Zahray, R. K., "Final Report
 Demonstration of Drilling Mud Waste-Wetland Soil Compatibility."

 July 1983, Shell Oil Co.
- Data from Subra Co. Waste Pits in Vermillion Parish. New Iberia,
 LA.
- 12. Twelve Month Interpretive Data Report on the St. Rosalie Site.

 Gulf South Research Institute, LA, Jan. 1977.
- 13. Collection and Analysis of Sediment Samples Maintenance Dredging Material, Navigation Projects. Mobile District, Corps of Engineers, Jan. 1977.
- 14. White, Kevin D. and Tittlebaum, Marty E., "Metal Distribution and Contamination in Sediments." ASCE, <u>Journal of Environmental</u>

 Engineering, April 1985.
- 15. Analysis of Water, Core Material, and Elutuate Samples Collected Near Buras, Louisiana. Harold L. Leone, Jr., U.S. Dept. of the Interior, Geological Survey, April 1977.
- 16. Analysis of Water, Core Material, and Elutuate Samples Collected Near New Orleans, Louisiana. U.S. Dept. of the Interior, Geological Survey, 1977.
- 17. Environmental Assessment for Unauthorized Forced Drainage Project. Environmental Industrial Research Associates, Inc., Metairie, LA, May 1984.
- 18. Winger, P. V. and Andreaseu, J. K., "Contaminant Residue in Fish and Sediments from Lakes in the Atchafalaya River Basin (Louisiana)." Archives of Environmental Contamination and Toxicology, 1985.

- 19. DeLaune, R. D., Reddy, C. N. and Patrick, W. H., Jr., "Accumulation of Plant Nutrients and Heavy Metals through Sedimentation Processes and Accretion in a Louisiana Salt Marsh." <u>Estuaries</u>, December 1981.
- 20. Research Triangle Institute Final Report Analysis of Metals and Organics in Sediment and Biota. March 18, 1985.
- 21. U.S. Army Engineers, Vicksburg District, Storet. U.S.

 Environmental Protection Agency, Washington, D.C., Oct. 1986.
- 22. U.S. Environmental Protection Agency Headquarters, Storet. Texas

 Data, Washington, D.C., Oct. 1986.
- Ecology and Environment, Inc., Dallas, Texas. Pit Sampling at D.L. Mud, Inc., Abbeville, LA, June, 1986.
- 24. Ecology and Environment, Inc., Dallas, Texas. Pit Sampling at D.L. Mud, Inc., Abbeville, LA, July, 1985.
- 25. Holder, S. W., Jr., "Selected Trace Elements in the Water, Sediment, Particulates and Estuarine Clam, <u>Rangia Cuneata</u>, from Lake Pontchartrain, Louisiana." M.S. Thesis, UNO, New Orleans, 1979.
- 26. Environmental Impact Statement Southwest Pass, Mississippi River Ocean Dredged Material Disposal Site Designation. EPA - Office of Water Criteria and Standard Division, Washington, D.C., Aug. 1984.
- 27. Heavy Metal Inputs to Mississippi Delta Sediments A Historical View. B. J. Presley, J. H. Trefry and R. F. Shokes, 1980.
- 28. Khalid, R. A., Gambrell, R. P., Taylor, B. A. and Patrick, W. H.,

 "Literature Survey of Reservoir Contaminant Problems," Laboratory

 for Wetland Soils and Sediment, Center for Wetland Resources, LSU,

 Contract No. DACW 39-80-C-0032, May 1983.

COMMENT LEGEND

- g. ppm (parts per million)
- h. elutriate data may be available
- i. other metal data may be available
- j. water column data may be available
- k. actual value is known to be less than value given
- 1. actual value is known to be greater than value given
- m. presence of material verified but not quantified. In the case of temperature or oxygen reduction potential, M indicates a negative value.
- n. mg/g (milligram per gram)

LIST OF SYMBOLS

Ag	silver	Fe	iron
Al	aluminum	Hg	mercury
As	arsenic	Mn	magnesium
Ва	barium	Ni	nickel
Ве	beryllium	Pb	lead
Cd	cadmium	Se	selenium
Со	cobalt	V	vanadium
Cr	chromium	Zn	zinc
Cu	copper		

6. BIBLIOGRAPHY

- Adams, R. B. and Parker, N. L., "In the Pits in Louisiana (Bayou Baby Blues)," Proceedings of the Second Water Quality and Wetlands Mgt. Conference, New Orleans, 1986.
- Alan, H., Director, Environmental Studies Inst., Drevel University Philadelphia, PA, Personal Communication, Nov. 1986.
- Andren, A. W. and Harriss, R. C., "Methylmercury in Estuarine Sediments," Nature, Vol. 245, No. 5423, 1973.
- Aswand, T., Amoco Oil, Regional Geologist, New Orleans, Personal Communication, Oct. 1986.
- Bagshani, G., Freeport Chemical, Research Dept., Belle Chase, LA, Personal Communication, Oct. 1986.
- Bernard, D. L., Univ. Southwestern La., Physics Dept., Lafayette, LA, Personal Communication, Nov. 1986.
- Besson, R. R., President, West Jefferson Levee District, Marrero, LA, Personal Communication, July 1986.
- Blood, T., USGS, Minerals Mgt. Service, Metairie, LA, Personal Communication, Oct. 1986.
- Bernard, D. L. and Roy, K. W., "Heavy Metals in Louisiana Crayfish (Procambarus clarkii) Determined by X-ray Fluorescence Analysis," Freshwater Crayfish, Vol. 3, 1977.
- Brotman, B., Environmental Professional Ltd., Metairie, LA, Personal Communication, Aug. 1986.
- Butz, T. R., et al., "Hydrogeochemical and Stream Sediment Detailed Geochemical Survey for Texas Gulf Coast," U.S. Dept. of Energy, Washington, D.C., 1980.
- Capozzoli, F, Capozzoli and Assoc., Baton Rouge, LA, Personal Communication, Dec. 1986.
- Carmouche, E. Ex, "Neutron Activation Analytical Determination of Trace Elemental Burdens in Species and Tissues," Masters Thesis, McNeese State University, Lake Charles, LA, 1983.
- Childress, G., University of Southeastern LA, Dept. of Biology, Hammond, LA, Personal Communication, Jan. 1987.
- Conference Publication, Geological Society of America, Southeastern Section, 32nd Annual Meeting, March 1983.
- Connell, D. W. and Miller, G. J., Chemistry and Ecotoxicology of Pollution, John Wiley and Sons, Inc., New York, 1984.

- Culp, J., Texaco Oil, Regulatory Compliance, New Orleans, Personal Communication, Oct. 1986.
- Draft Environmental Impact Statement, Proposed Oil and Gas Lease Sales 94, 98 and 102, Gulf of Mexico Region, Minerals Management Service, 1984.
- Dupont, D., Permit Agent, Terrebonne Parish, Personal Communication, July 1986.
- "Ecological Investigation of Petroleum Production Platforms in the Central Gulf of Mexico," Vol. I, Part 4 & 5, Southwest Research Institute, San Antonio, TX, 1981.
- Fike, E., CZM Coordinator, Lafourche Parish Council, Thibodaux, LA, Personal Communication, July 1986.
- Flowers, E., Tulane University, New Orleans, LA, Personal Communication, July 1986.
- Francinques, A., Assistant Chief Engineer, Orleans Levee District, New Orleans, LA, Personal Communication, July 1986.
- Freeman, B. D. and Devel, L. E., "Closure of Freshwater Base Drilling Mud Pits in Wetland and Upland Areas," Proceedings of a National Conference on Drilling muds, Norman, OK, 1986.
- Freeman, B. D. and Devel, L. E., "Guidelines for Closing Drilling Waste Fluid Pits in Wetland and Upland Areas," Part I, II & III.
- Frey, F. P., "Disposal of Drilling Discharges on Land and Offshore."
- Folsom, R., et al., "Influence of Disposal Environment on Availability and Plant Uptake of Heavy Metals in Dredged Material," Technical Report EL-81-12, U.S. Army Engineer Waterways Experiment Station, Environmental Laboratory, Vicksburg, MS, Dec. 1981.
- Forman, W., Freeport McMoran, Corporate Environmental Engineer.
- Gambrell, R. P., Reddy, C. N. and Khalid, R. A., "Characterization of Trace and Toxic Materials in Sediments of a Lake being Restored,"

 Water Pollution Control Federation Journal, Vol. 55, No. 9, Sept. 1983.
- Garrison, C., U.S. Geological Survey, Baton Rouge, LA, Personal Communication, Nov. 1986.
- Gosselink, J. G., "Ecology of Delta Marshes of Coastal Louisiana: A Community Profile," Center for Wetland Resources, LSU, May 1984.
- Gouguet, R., Department of Wildlife and Fisheries, Seafood Office, Baton Rouge, LA, Personal Communication, Jan. 1987.

- Grantham, C. K. and Sloan, J. P., "Toxicity Study Drilling Fluid Chemicals on Aquatic Life," Proceedings, Environmental Aspects of Chemical Use in Well Drilling Operations, Houston, TX, 1975.
- Greene, I., Mobil Oil Co., Regulatory Functions, Lafayette, LA, Personal Communication, Nov. 1986.
- Heitman, J. F., "Chemical Stratification and Environmental Concerns of Oklahoma Offsite Disposal Pits," Proceedings of a National Conference on Drilling Muds, Norman, OK, 1986.
- Henington, B., Mobil Oil, Paleoentologist, New Orleans, LA, Personal Communication, Oct. 1986.
- Hull, F., Corps of Engineers, Planning Division, New Orleans District, New Orleans, LA, Personal Communication, July 1986.
- Isphording, W. C., Flowers, G. C. and Stringfellow, S. A., "Comparison of Heavy Metal Partitioning Behavior from Bays and Estuaries of the Northern Gulf Coast," University of S. Alabama, Mobile, AL, American Geophysical Union, 1984 Fall Meeting, San Francisco.
- Isphording, W. C., Stringfellow, J. A. and Flowers, G. C., "Sedimentary and Geochemical Systems in Transitional Marine Sediments in the Northeastern Gulf of Mexico," Transactions, Gulf Coast Association of Geological Societies, Vol. XXXV, 1985.
- Isphording, W. C., University of S. Alabama, Mobile, AL, Personal Communication, Nov. 1986.
- Khalid, R. A., Gambrell, R. P., Verloo, M. G. and Patrick, W. H., Jr., "Transformations of Heavy Metals and Plant Nutrients in Dredged Sediments as Affected by Oxidation Reduction Potential and pH," Louisiana Agricultural Experiment Station, LSU, May 1977.
- Klaassen, C. D., Amour, M. O. and Dovll, J., <u>Toxicology</u>, MacMillian Publishing Co., New York, 3rd Ed., 1986.
- Lashover, J., Kaiser Aluminum, Environmental Engineer, Grammercy, LA, Nov. 1986.
- Lee, C. R. Smart, R. M., Sturgis, T. C., Gordon, R. N., Sr., and Landin, M. C., "Prediction of Heavy Metal Uptake by Marsh Plants Based on Chemical Extraction of Heavy Metals from Dredged Material," U.S. Army engineer Waterways Experiment Station, Environmental Effects Laboratory, Vicksburg, MS, Technical Report D-78-6, 1978.

1

Lee, R., Waterways Experiment Station, COE, Vicksburg, MS, July 1986.

- Lindaui, C. W., Texas A & M, Nov. 1986.
- Lo, Environmental Industrial Research Inc., Metairie, LA, Personal Communication, July 1986.
- Luzes, C. L., Plaquemines Parish Environmental Services, Braithewaite, LA, Personal Communication, July 1986.
- Lytle, T. F. and Lytle, J. S., "Heavy Metals in Oysters and Clams in St. Louis Bay, Mississippi," Bulletin of Environmental Contamination and Toxicology, Vol. 29, 1982.
- Lytel, T., Gulf Coast Research Lab, Ocean Springs, MS, Personal Communication, Jan. 1987.
- Mahloch, J., Waterways Experiment Station, Army Engineers, Vicksburg, MS, Personal Communication, July 1986.
- "Management of Bottom Sediments Containing Toxic Substances,"

 Proceedings of the U.S.-Japan Experts Meeting (5th) held at New
 Orleans, LA, on Nov. 1979, National Heart, Blood and Lung
 Institute, Bethesda, MD, Sept. 1980.
- Montalvo, J. G., Jr., and Brady, D. V., "Concentrations of Hg, Pb, Zn, Cd and As in Timbalier Bay and the Louisiana Oil Patch," Gulf South Research Institute, 1979.
- Monaghan, P. H., McAuliffe, C. D. and Weiss, F. T., "Environmental Aspects of Drilling Muds and Cuttings from Oil and Gas Extraction Operations in Offshore Coastal Waters," Proceedings, Offshore Technology Conference, 1977.
- Moseley, H. R., "Summary of API Onshore Drilling Mud and Produced Water Environmental Studies."
- McClelland Engineers, New Orleans, LA, Personal Communication, Nov. 1986.
- McDonald, B., USEPA, Region 6, Dallas, TX, Personal Communication, July 1986.
- National Ecosystem Team, Slidell, LA, U.S. Dept. of Wildlife and Fisheries, Personal Communication, Dec. 1986.
- Patrick, W. H. and Turner, F. T., "Effect of Redox Potential on Manganese Transformation in Waterlogged Soil," <u>Nature</u>, Vol. 220:5166, Nov. 1968.
- Patrick, W. H., Jr., Reddy, C. N. and DeLaune, R. D., "Accumulation of Plant Nutrients and Heavy Metals through Sedimentation Process and Accretion in a Louisiana Salt Marsh," <u>Estuaries</u>, Vol. 4, No. 4, 1981.

- Perez, U.S. Coast Guard, Port Safety Pollution Response, Personal Communication, June 1986.
- Pizzolotto, V., Dept. of Transportation and Development, Baton Rouge, LA, Personal Communication, Nov. 1986.
- Reimers, Tulane University, Dept. of Environmental Health, New Orleans, LA, Personal Communication, July 1986.
- Sabins, D., Office of Water Resources, Dept. of Environmental Quality, Baton Rouge, LA, Personal Communication, Nov. 1986.
- Schurtz, M. H. and St. Pe, K. M., "Water Quality Investigation of Environmental Conditions in Lake Pontchartrain Report on Interim Findings," Louisiana Dept. of Environmental Quality, April 1984.
- "Sediment Quality Criteria Methodology Validation, Calculation of Screening Level Concentrations from Field Data," USEPA Criteria and Standards Division, Washington, D.C., July 1986.
- Simmers, J. W., Folsom, B. L., Jr., Lee, C. R. and Bates, D. J., "A Field Survey of Heavy Metal Uptake in Naturally Occurring Saltwater and Freshwater Marsh Plants," Technical Report EL-81-5, U.S. Army Engineer Waterways Experiment Station, Environmental Lab., Vicksburg, MS, June 1981.
- Smith, G. W. and Field, M. M., "Water Management Considerations for Gulf Coast Nonhazardous Oilfield Waste Management Facilities," Proceedings, National Conference on Drilling Muds, Norman, OK, 1986.
- "The National Estuarine Pollution Study, Vol. II A Report to the Congress," U.S. Dept. of Interior, Federal Water Pollution Control Administration, Nov. 1969.
- "Trace and Toxic Metal Uptake by Marsh Plants as Affected by Eh, pH and Salinity," Center for Wetland Resources, LSU, Dec. 1977.
- Trefry, J. H., Merry S. and Trochine, R. P., "Geochemical Cycles of Cadmium and Lead for the Mississippi River and Delta," Fla. Inst. of Technol., Melbourne, FL, American Geophysical Union, 1984 Ocean Sciences Meeting, New Orleans, LA, 1984.
- University of New Orleans, Bio-organic Studies, New Orleans, LA, Personal Communication, July 1986.
- Van Beek, H., Coastal Environments, Inc., Baton Rouge, LA, Personal Communication, Dec. 1986.
- Vincent, R., The Ecology Center of New Orleans, Inc., Personal Communication, July 1986.
- Wakeman, T. H., "Chemical and Biological Mobilization of Heavy Metals from Estuarine Sediments," Proceedings from the Third Federal Interagency Sedimentation Conference, 1976.

et. Ph.

- Warren, J., U.S. Army Engineers, Hydraulics Section Engineering Division, New Orleans, LA, Personal Communication, July 1986.
- Water Quality Analysis, La. Dept. of Transportation and Development, Office of Highways, State Project #700-08-61, Relocation of US 90 Morgan City to LA 311 St. Mary, Assumption and Terrebonne Parish, 1980.
- Weldon, D., Exxon Co., Regulatory Compliance, New Orleans, LA, Personal Communication, Nov. 1986.
- Welsh, J., Surface Mining Division, Office of Conservation, La. Dept. of Natural Resources, Baton Rouge, LA, Personal Communication, Nov. 1986.
- Wheeland, T., Woodward-Clyde, Baton Rouge, LA, Personal Communication, Dec. 1986.
- Wood, B. K. and Trefry, J. H., "The Distribution and Provenance of Trace Elements in Eastern Gulf of Mexico Sediments," Fla. Inst. of Technol., Melbourne, FL, Transaction, Gulf Coast Association of Geological Societies 30th Annual Meeting, Oct. 1983.
- Young, D., National Space Technology Lab, Bay St. Louis, MS, Personal Communication, Jan. 1987.
- Zarba, C., Criterion Standards Division, Office of Water Regulations and Standards, Criteria and Standards Division, Environmental Protection Agency, Washington, DC, Personal Communication, Sept. 1986.

APPENDIX C

Excursions from USGS Sediment Alert Levels and Statewide Order 29-B Limitations

Sites and Metals Exceeding USEPA Region 6 Sediment Alert Levels:

sa.6 Cd 80010.00

Sites and Metals Exceeding Statewide Order 29-B Sec. 2.7.C.2 Limitations

san.2 Cd 10.00k	so.5 As 10.00
sa.2 Cd 100.00 Pb 3500.00	ho.1 As 37.5k
As 20.00 sa.6	sp.4 As 10.00
As 11.00 As 10.00 Pb 2500.00 Cd 80010.00	sp.5 As 12.20
sca.2 As 15.00	sp.7 As 11.00
sca.5 As 12.00	cp.1 As 12.00 Cd 10.00k
sca.6 As 12.00	cp.2 As 12.00 Cd 10.00k
sca.7 As 10.00	cp.3 Cd 10.00k
sca.8 As 11.00	cp.4 Cd 10.00k
rtca.4 As 10.0k Se 20.0k	cp.5 Cd 10.00k
rtca.5 As 87.1 Se 20.0k	cp.6 Cd 10.00k
rtca.7 As 12.8	cp.7 As 12.00 Cd 10.00k
rtca.9 Se 26.3	ср.8 Cd 10.00k

	rtca.10 16.2 124.0 20.0k	As Se	rtp.1 58.2 20.0k
Se	rtca.11 34.9	As	sb.3 10.00
	rtca.12 10.2	As As	sb.5 12.00 15.00
As Cd			sb.6 10.00
As Cd	11.00 10.00k	As	sb.7 10.00
Cd As	sc.5 16.00 10.00k 13.00 10.00k		sb.13 10.00 10.00k
As Cd As	10.00k	As	sb.14 11.00 sb.15
Cd		As	10.00 10.00k
	sc.7 16.00		sb.16 10.00 10.00k
As	sc.8 14.00		sch.1
	5C.9 19.00 10.00k	Cd	10.00
As	sc.10 23.00	As	hch.1 37.9k
As	sc.11 22.00	Cd	sjm.3 10.00k
Λ	sc.12	Cd	smn.3 10.00k

As 10.00

	50.13 15.00	As	smn.4 11.00 10.00k
	sc.14 19.00		smn.9 10.00k
As Cd	sc.15 14.00 10.00k		smn.10 10.00k
	13.00 10.00k		smn.13 10.00k
Cd	10.00k 10.00k		smn.15 10.00k
	sc.17 13.00		smn.16 10.00k
Cd	sc.18 10.00k 12.00		smn.17 10.00k
	10.00k	As	smn.18 10.00 10.00k
As	17.00	L.U.	TO TOOK
	sc.20 13.00		smn.20 10.00k
As	sc.21 18.00		sm.6 10.00k
As	sc.22 14.00		sm.7 10.00k
	sc.23 14.00		sm.10 14.00
As	sc.24 15.00		sm.12 10.00k
	sc.26		sm.13 10.00k

As 16.00

As	sc.28 11.00 10.00k		sm.14 10.00k
	sc.29		sm.18 10.00k
Cd Cd	10.00k 10.00k		rtm.1 22.2
	sc.33 10.00L	As	rtm.2 10.0k
	sc.38 13.00		20.0k rtm.3
	sc.39 10.00	As As Se	13.1 70.1 20.0k
	sc.40 12.00		sty.1 10.00k
Cd	sc.42 10.00L		sty.2 10.00k
	sc.43 10.00L	Cd	sty.3 10.00k
Cd	sc.50 10.00k 10.00k		sty.4 10.00k
As	sc.51 12.00	Cd	cty.1 10.00k
Cd As		As	hty.1 38.0k
As Se As Se	rtc.1 10.0 48.9 10.0k 20.0k	As	hty.2 38.6k
• ⊅ €	discrete at No. 17.	As	hty.3 38.6k

	si.1		
Δœ	10.00		
Cet	10.00k		made 1
(-(1	10.00k	en. 1	st.1
		Cd	10.00k
	si.2		
	10.00k		st.2
	2 C 8 C C 10	As	
		Pb	
	si.3		540.00
As			
Cd			17.00
	10100	Pb	
As		2n	560.00
Ca	10.00		
			st.3
	si.4	Δσ	11.00
	10.00	Cd	
	10.00		17.00 k
i-1 1:25	10.00		
		Cd	10.00k
	si.5		
	12.00		st.4
Cd			21.00
Δe	10.00		32.00
Cd	10.00	11/	Contradence de Contrade
	10,00		
			st.5
	si.6	As	10.00
As	15.00		
Cd	10.00		
	17.00		st.6
	10.00	As	10.00
	and the factor	,,2	at the a tour tour
	si.7		st.7
Cd	10.00k	As	16.00
	si.10		st.10
Cd	10.00k	Λ,	13.00
Cu	10.00k	m =	10.00
	si.8		st.11
Cd	10.00k	As	
Pb	5000.00	· /	
As	10.00		
As	10.00		st.12
	MAC THE SECTION	As	
		As	
	sj.1	ri =>	as as a Natival
As	11.00		
	10.00		ct.3
F1 20	action actions	As	12.00L
		ri ==	and a series services have

sj.2 As 12.00 As 12.00 As 13.00	ct.4 As 12.00L
sj.3 As 10.00 As 13.00 As 13.00	eirt.1 Cd 200.00k Hg 688.00k Pb 15400.00k Zn 71800.00k
sj.7 As 10.00	eirt.2 Cd 410 Hg 178 Pb 500k Zn 65700
As 14.00	
cj.1 As 11.00 As 13.00	eirt.3 Cd 420 Hg 180 Pb 12700 Zn 144100
cj.2 As 12.00 As 10.00	eirt.4 Cd 420 Hg 180 Pb 12700
hj.1 As 39.0k	Zn 144100
hj.2 As 39.1k	rtt.1 Se 49.8 As 49.5 Se 20.0k
hj.3 As 40.3k	rtt.2 Cd 603
hj.4 As 40.1k	rtt.4 As 10.7 Se 67.0
hj.5 As 122k	As 12.3 As 10.0k Se 20.0k
hj.6 As 112k	rtt.5 Se 38.4 As 49.8
hj.7	Se 20.0k

hj.7 As 116k

20.0k

Se

		stx	. 1
	sla.3	As 1	7.00
Cd	10.00k	As 30	5.00
	10.00k		5.00
	23.00	As 2	
,	### 147 # 147	ns £	3 a 4.44
	S1.1		***
		stx	
	11.00	Cd 19	D.OOL
Ud	10.00k		
		stx	
	sl.4	As 2:	2.00
As	16.00		
As	14.00		
		stx	.10
		As 1	
	sl.5		
	10.00		
r-1 ::5	10100		4 ~
		stx	
	1 /	As 2	0.00
	sl.6		
As	10.00	•	
		sv.	
		As 1	4.00
	s1.7	Cd 1	0.00k
Cd	10.00k	As 1	1.00
		Cd 1	
		-	
	s1.10		
	51.IU		
		cv '	7
	14.00	SV	
		As 1	4.00
	14.00		4.00
As	14.00 sl.11	As 1	4.00
As As	14.00 51.11 12.00	As 1 Cd 1	4.00 0.00k
As As	14.00 sl.11	As 1 Cd 1	4.00 0.00k 3
As As	14.00 51.11 12.00	As 1 Cd 1 sv. As 2	4.00 0.00k 3 1.00
As As	14.00 sl.11 12.00 11.00	As 1 Cd 1 sv. As 2	4.00 0.00k 3
As As As	14.00 sl.11 12.00 11.00	As 1 Cd 1 sv. As 2	4.00 0.00k 3 1.00
As As As	14.00 51.11 12.00 11.00 rt1.1 404.0	As 1 Cd 1 sv. As 2	4.00 0.00k 3 1.00
As As As Cd Se	14.00 51.11 12.00 11.00 rt1.1 404.0 50.6	As 1 Cd 1 sv. As 2	4.00 0.00k 3 1.00 0.00k
As As As	14.00 51.11 12.00 11.00 rt1.1 404.0 50.6	As 1 Cd 1 SV. As 2 Cd 1 SV.	4.00 0.00k 3 1.00 0.00k
As As As Cd Se Cd	14.00 51.11 12.00 11.00 rtl.1 404.0 50.6 703.0	As 1 Cd 1 SV. As 2 Cd 1 SV. As 2	4.00 0.00k 3 1.00 0.00k 4 5.00
As As As Cd Se	14.00 \$1.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k	As 1 Cd 1 SV. As 2 Cd 1 SV. As 2	4.00 0.00k 3 1.00 0.00k
As As Cd Se Cd As	14.00 51.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k	As 1 Cd 1 SV. As 2 Cd 1 SV. As 2	4.00 0.00k 3 1.00 0.00k 4 5.00
As As Cd Se Cd As	14.00 \$1.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k	As 1 Cd 1 Sv. As 2 Cd 1 Sv. As 2 Cd 1	4.00 0.00k 3 1.00 0.00k 4 5.00
As As Cd Se Cd As	14.00 51.11 12.00 11.00 rt1.1 404.0 50.6 703.0 10.0k 20.0k	As 1 Cd 1 sv. As 2 Cd 1 sv. As 2 Cd 1	4.00 0.00k 3 1.00 0.00k 4 5.00 0.00k
As As Cd Se Cd Se	14.00 \$1.11 12.00 11.00 rt1.1 404.0 50.6 703.0 10.0k 20.0k	As 1 Cd 1 SV. As 2 Cd 1 SV. As 2 Cd 1	4.00 0.00k 3 1.00 0.00k 4 5.00 0.00k
As As Cd Se Cd As	14.00 51.11 12.00 11.00 rt1.1 404.0 50.6 703.0 10.0k 20.0k	As 1. Cd 1. Sv. As 2. Cd 1. Sv. As 2. Cd 1. Cd 1	4.00 0.00k 3 1.00 0.00k 5.00 0.00k
As As Cd Se Cd Se	14.00 \$1.11 12.00 11.00 rt1.1 404.0 50.6 703.0 10.0k 20.0k	As 1. Cd 1. Sv. As 2. Cd 1. Sv. As 2. Cd 1. Cd 1. As 1. Cd 1. As 1. Cd 1. As 1.	4.00 0.00k 3 1.00 0.00k 5.00 0.00k 5.00 0.00k 2.00
As As Cd Se Cd Se	14.00 51.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k 20.0k	As 1. Cd 1. Sv. As 2. Cd 1. Sv. As 2. Cd 1. Cd 1. As 1. Cd 1. As 1. Cd 1. As 1.	4.00 0.00k 3 1.00 0.00k 5.00 0.00k
As As Cd Se Cd As Se	14.00 51.11 12.00 11.00 rt1.1 404.0 50.6 703.0 10.0k 20.0k	As 1. Cd 1. Sv. As 2. Cd 1. Sv. As 2. Cd 1. Cd 1. As 1. Cd 1. As 1. Cd 1. As 1.	4.00 0.00k 3 1.00 0.00k 5.00 0.00k 5.00 0.00k 2.00
As As Cde Cdas As As	14.00 sl.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k 20.0k	As 1 Cd 1 SV. As 2 Cd 1 SV. As 2 Cd 1 Cd	4.00 0.00k 3 1.00 0.00k 5.00 0.00k 5.00 0.00k
As As Cde Cdas As As	14.00 51.11 12.00 11.00 rt1.1 404.0 50.6 703.0 10.0k 20.0k	As 1 Cd 1 SV. As 2 Cd 1 Cd	4.00 0.00k 3 1.00 0.00k 4 5.00 0.00k 5.00 0.00k
As As Cde Cdas As As	14.00 sl.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k 20.0k	As 1 Cd 1 SV. As 2 Cd 1 Cd	4.00 0.00k 3 1.00 0.00k 4 5.00 0.00k 5.00 0.00k 2.00 0.00k
As As Cde Cdas As As	14.00 sl.11 12.00 11.00 rtl.1 404.0 50.6 703.0 10.0k 20.0k	As 1 Cd 1 SV. As 2 Cd 1 Cd	4.00 0.00k 3 1.00 0.00k 4 5.00 0.00k 5.00 0.00k

As	50.11 11.00 10.00k	As	sv.7 3 16.00
As	so.13 10.00 10.00k	As	d 10.00k sv.8 s 15.00 d 10.00k
Cd	so.14 10.00k 10.00	A	5v.9 5 23.00
Cd	so.16 10.00k		d 10.00k sv.10
Cd	so.17 10.00k		5 19.00 d 10.00k d 10.00k
	so.18 10.00k	A: C:	sv.11 s 11.00 d 10.00k d 10.00k
Cd	so.19 10.00k		sv.13
Cd	so. 20 10.00k	A	s 13.00 d 10.00k s 18.00 d 10.00k
As	so.21 15.00 16.00	A	ev.2 a 2500.00 s 20.00 a 8600.00
Cd	so.23 10.00k		n 1600.00
Cd	50.24 10.00k	B Z	ev.3 s 10.00 a 2500.00 n 1100.00 s 71.00
Cd		C P	a 10000.00 d 11.00 b 1100.00 n 7800.00
As	11.00		rtv.1 de 42.6 s 11.8

